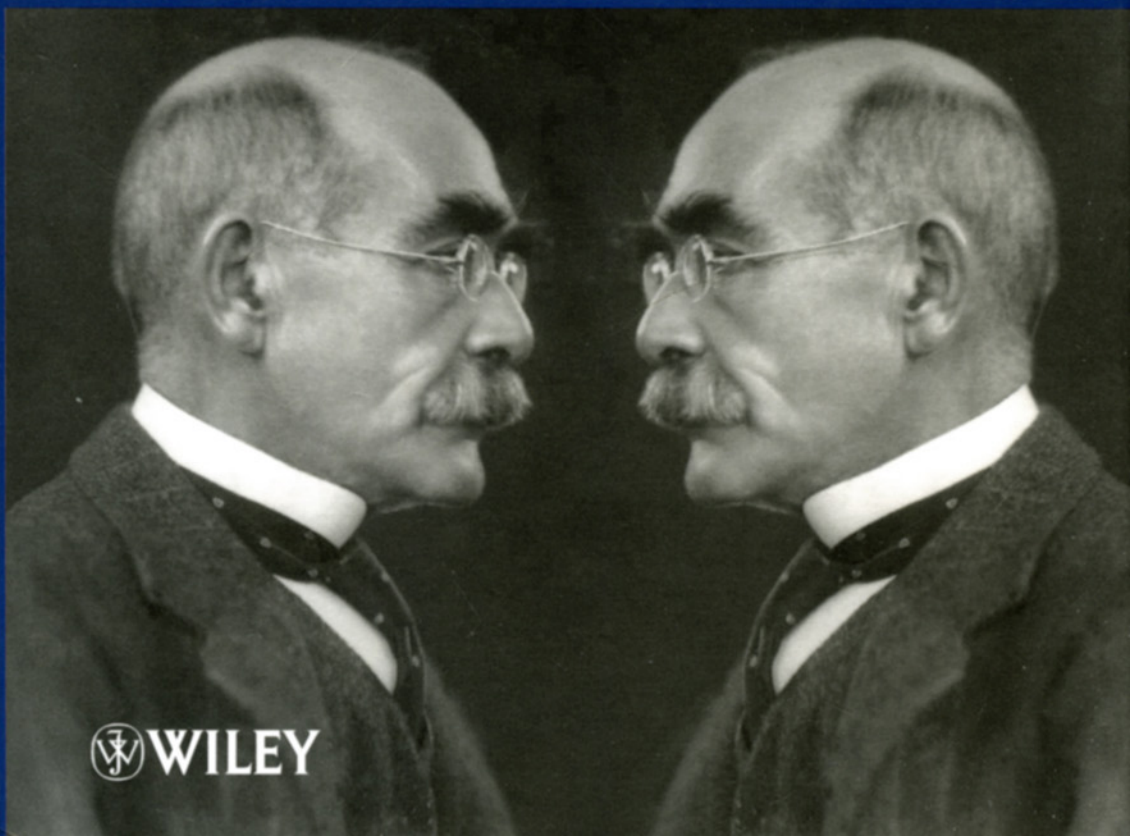
MOLTEN SALTS AND IONIC LIQUIDS

NEVER THE TWAIN?

Edited by
MARCELLE GAUNE-ESCARD
KENNETH R. SEDDON



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Never the Twain?

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MARCELLE GAUNE-ESCARD

KENNETH R. SEDDON

EUCHEM CONFERENCES ON MOLTEN SALTS

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PREFACE

Between Sunday 17th September 2006 and Friday 22nd September 2006, a meeting of major significance occurred in Hammamet, Tunisia: the 21st meeting of a series of EuChem Conferences on Molten Salts (for a comprehensive list, see preceding page). Not only did the 21st meeting have a metaphorical significance—a coming of age—but it marked a change in focus and title for the meetings. No longer the EuChem Conferences on Molten Salts, they were relaunched, phoenix-like, as the EuChem Conferences on Molten Salts and Ionic Liquids. This was a result of a long series of private conversations with many key figures, which culminated in an editorial (reproduced on the following pages) in *Molten Salts Bulletin* (**2005,** *85*, 1–3). A gauntlet had been thrown down. To condense the arguments: Molten salts and ionic liquids are both liquid salts containing only ions—they are thus the same subject. All that is different is the temperature! Both fields involve the study of Coulombic fluids for academic and industrial purposes, both employ the same principles, both require skilled practitioners (but high temperature systems require greater skills), both speak the same language; all that is different is image, and how superficial is that? There is so much knowledge, both empirical and theoretical, which can be passed from the molten salt community to the ionic liquid community, and *vice versa*. The gauntlet was picked up, and the result was the Hammamet meeting, and this book. We believe this meeting has catalysed a *rapprochement* between the two communities: East has met West, the peaches have touched, the brooklets have mingled, and the Montagues and the Capulets are reunited. Both fields are now stronger for this, and the future meetings are assured to be the prime focus for renewing these exchanges.

Whilst representing some of the key talks at the meeting, this book also provides discussion on the transfer of experimental methods and techniques between the differing temperature régimes. While it is conventionally invidious to highlight specific chapters, the reviews from Austen Angell, Keith Johnson, Richard Pagni, and George Papatheodorou are remarkable for their depth of insight and breadth of pedagogic experience, while the chapter from Tsutomu Sada shows the way forward to the industrialisation of products based on this new technology. We believe this book will also act as a line in the sand—the contents are a snapshot of a strengthened field. The tears of the phoenix are said to contain the healing abilities of purity, and its cry is said to be a beautiful song. May it long continue to sing, and may we be aware enough to listen.

MARCELLE GAUNE-ESCARD

KENNETH R. SEDDON

EDITORIAL

NEVER THE TWAIN ?

Oh, East is East, and West is West, and never the twain shall meet,
Till Earth and Sky stand presently at God's great Judgment Seat;
But there is neither East nor West, Border, nor Breed, nor Birth;
When two strong men stand face to face,
tho' they come from the ends of the earth!

—Rudyard Kipling, *The Ballad of East and West* (1889)

Marcelle has asked me to write a personal editorial for *Molten Salts Bulletin,* and so I am taking her at her word. It will be personal, and hence it will be polemical. And I take as my subject the unfortunate, nay potentially disastrous, split which has emerged between the (high temperature) molten salt community (East) and the (low temperature) ionic liquid community (West). I will argue that this is destructive, cliquish, petty, and (if continuing) will result in the loss of key skills to the whole community. I do not want to wait until Judgement Day for the strong men (and women) of both camps to stand face to face!

I had the honour and privilege of being introduced to low-temperature molten salts, henceforth referred to as ionic liquids, by the fathers of the field–Chuck Hussey and John Wilkes. I was able to learn at the feet of the experts, in depth, the practical and theoretical aspects of ionic liquids, including much unpublished information. In other words, they taught me the tricks of the trade, with enthusiasm and generosity. It led to years of fruitful collaboration with Chuck, and my introduction into the molten salts community. This was dominated by the grandfathers of the field, Bob Osteryoung and Gleb Mamantov. Now, from my experience in the field of second-harmonic generation, whose practitioners were (by and large, but not universally) mean-minded, self-obsessed *prima donnas,* who treated newcomers as potential threats. I had steeled myself for a similar response from the molten salt community. Never had I been more wrong. I was immediately drawn to the core of the subject, and Bob and Gleb (intellectual giants) could not have been more welcoming to a tyro, and immensely generous with both their time and advice. And then there were the conferences: the Gordon Conferences, the Molten Salt Sessions at the Electrochemical Society meetings, the EUCHEM meetings, the Molten Salt series, and the Molten Salts Discussion Group (MSDG). And, as a zenith, the NATO ASI meeting in Camerino,

*From *Molten Salts Bulletin*, **85** 1–3 (2005).

two weeks in which all the key people in the field came together to teach the students and post-doctoral fellows. But it is now 2005, and I feel I could be writing an obituary for molten salts: the Gordon meetings were cancelled for lack of support, the Molten Salts meetings (the latest being MS7) will be lucky to have enough participants to be viable, the subject appears to be controlled by cliques, and the MSDG looks like a talking shop for the formerly active. And attending the lectures was intense *déjà vu* — lectures which contained little new content given by the same tired faces. And, most worrying, most of the highly skilled and imaginative practitioners (e.g., Øye, Angell, Freyland, Papatheodorou, Johnson, Gaune-Escard. Bjerrum, etc.) are approaching, or have passed, retirement age.

In contrast, the cheeky interloper, ionic liquids, which was lucky to get one session in ten in a molten salts meeting, which had very few practitioners, and which had no industrial track record, has gone from strength to strength. In June 2005, the first International Congress on Ionic Liquids (COIL) was held in Salzburg, with 410 participants; there have been three ten-session symposia at the ACS National meetings (San Diego, 2001; Boston, 2002; New York, 2003), each being the most attended sessions at their respective meeting; and a NATO ARW in Crete in 2000. The number of published papers on ionic liquids has risen from 20 in 1994 to over 1000 in 2004, and according to the independent ISI web site (http://www.esi-topics.com/ionic-liquids/index.html) there have been papers from 3342 authors in 57 countries, published in 290 journals, from 745 institutions. Tracking the open literature publications, patents in the area are also increasing exponentially, and industrial interest is burgeoning (BASF, DeGussa, Eastman Chemicals, and Iolitec already have commercial processes operating) and there are many large-scale suppliers (including Merck, Cytec, C-TRI, SACHEM, and BASF). Ionic liquids have captured the imaginations of the whole chemical (and, indeed, biochemical and physics) community, in a way that molten salts never did. But it is the same subject!! All that is different is the temperature! Both fields involve the study of Coulombie fluids for academic and industrial purposes; both employ the same principles; both require skilled practitioners (but high temperature systems require greater skills); both speak the same language (unlike the Americans and the British!!); all that is different is image, and how superficial is that?

So what has gone wrong – it is not clear when the twain stopped meeting, and why they are still separated. Maybe it is psychology, maybe personalities, maybe nomenclature. Marcelle—why is this the *Molten Salts Bulletin,* and not the *Ionic Liquids and Molten Salts Bulletin?* Why is MS7 not MS1L7? Why is MSDG not ILDG? It is not through lack of excellent and prominent people straddling the divide (viz. Johnson, Fehrmann, Boghosian. Angell. and Freyland (who gave a fascinating talk at COIL)). There is so much knowledge, both empirical and theoretical, which can be passed from the molten salt community to the ionic liquid community, and *vice versa.* WHY IS IT NOT HAPPENING? Any unbiased observer would note two immiscible groups, with a slightly fuzzy interface. I will lay my cards on the table—I want a homogeneous single phase. Am I a voice in the wilderness? I don't think so! I believe that the members of both communities for whom I have the greatest respect all feel the same way. Are we condemned to be Montagues and Capulets? Do we want to say

"Good night, good night! Parting is such sweet sorrow"? Is nomenclature going to keep us apart (***"What's in a name? That which we call a rose by any other name would smell as sweet"***)? Do we accept that "***What must be shall be***"? I would prefer to think that "***Such young unfurrowed souls roll to meet each other like two velvet peaches that touch softly and are at rest; they mingle as easily as two brooklets that ask for nothing but to entwine themselves and ripple with ever-interlacing curves in the leafiest hiding-places***." (George Eliot, *Adam Bede*. 1859). So, I implore you all, reverse history, and enjoy the fruits of remingling. I suggest we seek funding from EUCHEM to bring about a joint meeting to map the way forward: Marcelle – that is one with your name on it!

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Hoc erat in votis. Let us attempt to merge East and West together Ken. And let it be in 2006.

MARCELLE

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1 Ionic Liquids in the Temperature Range 150–1500 K: Patterns and Problems

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Abstract

In this chapter we trace some of the developments in ionic liquids physical chemistry from the crimson metal–molten salts of Humphrey Davy's original melt electrolysis discoveries of elements, to the newest ambient-to-200 °C fuel cell electrolytes. We discuss the origin of a common pattern of behaviour for ionic liquids as they are cooled down, often reaching the glassy state—a pattern that extends from the liquid orthosilicates of the earth's mantle to the subambient temperature ionic liquids of the present era. However, where glasses are rare among orthosilicates and are generally limited to the complex anion "polymerised" silicate liquids (Bockris's "island anions"), they are the general result of cooling the ambient ionic liquids of current interest, even though the anions are always simple. How to maintain high fluidity along with low vapour pressure is the challenge. The highest ambient temperature fluidities are obtained with ionic liquids of the proton transfer variety, and they rival aqueous solutions in conductivity—a consequence of optimising Coulomb cohesion and charge carrier concentration in the absence of solvent. These protic ionic liquids (PILs) show much promise as fuel cell electrolytes and also as biopreservatives. We illustrate the great range of electrolyte character that can be obtained with PILs, using an energy level diagram for proton transfers, and then compare the fuel cell performances of electrolytes of organic cations with that of their inorganic cation cousins.

Molten Salts and Ionic Liquids: Never the Twain? Edited by Marcelle Gaune-Escard and Kenneth R. Seddon

1.1 INTRODUCTION

It is now a little over 200 years since Sir Humphrey Davy, in England, first saw the deep crimson colour of sodium metal dissolved in molten sodium chloride [1]. He was in the process of using electrochemically driven decomposition to produce, for the first time, a free alkali metal element and was observing the consequence of some dissolution of the liberated metal in the liquid salt. This followed Volta's invention of the voltaic "pile" that provided the driving force for the decomposition, by only a few years (which this author finds remarkable).

We select three particular themes to highlight as we follow developments in understanding of ionic liquids from Davy's time to the present era. The themes are (1) ionic liquids that are coloured as a result of particular light-absorbing structural features, (2) ionic liquids providing interconversion of chemical and electrical forms of energy, and (3) ionic liquids transforming to glassy solids in consequence of failure to crystallise. Presently, the low temperature versions of Davy's liquids are being found useful in fuel cells that permit the reverse of Davy's process—namely, the release of electrical energy by conversion of elements (hydrogen and oxygen) to the chemically combined state (water). The narrative will be brief and sweeping and will be strongly and transparently stamped by the author's personal experience over a fifty year period of research in ionic liquids. It is by no means intended to be an account of the field of ionic liquids as a whole.

When the writer was a graduate student in chemical metallurgy at Melbourne University in the 1950s, the understanding of silicate liquids of metallurgical relevance was in a primitive state. Although molten calcium magnesium silicates had long been used in the production of iron by a chemical reduction process (using carbon as the source of electrons to liberate the metal from its combined state), the literature of the time mostly referred to the high temperature liquids in terms of *molecules* of the chemical compounds from which they were formed. Thus the furnace slag contained MgO molecules, CaO molecules, and SiO_2 molecules. In a radical departure from the thinking of the time, John Bockris at Imperial College had recently [2, 3] launched the idea that these highly fluid materials actually consisted of free cations of the alkaline earth elements moving in a sea of silicate anions of varying complexity. The writer's M.Sc. supervisor, thermodynamicist Mervyn Willis [4, 5], liked the idea and encouraged him to accept a fellowship in Bockris's new laboratory in the United States at the University of Pennsylvania. At that time, a subfield of Bockris's "ionic liquids"—one that was designated "molten salts" (because they were more simply constituted than the molten silicates)—was under intense investigation. This was because of the molten-salt-cooled nuclear reactor project that was then under development at Oak Ridge National Laboratory. The reactor was very successfully using molten alkali fluorides and fluoroberyllates as the medium for heat transfer between reactor and turbine. (After highly successful demonstrations, this project was moth-balled in the 1960s as doubts about the future of nuclear energy arose, but it may well be resurrected in the present climate of crisis consequent on the threat posed by carbon energy based global warming.)

Harry Bloom, from the University of Hobart in Tasmania, Australia, was a visiting scientist in Bockris's laboratory. As a student at Melbourne University, Bloom had studied complex anions in molten salts [6] under displaced German physical chemist Erich Heymann, who had come from the early German school of molten salt chemists. The problem of identifying complex anions (like $[CdCl_4]^{2-}$ that, in aqueous solutions, moved toward the anode in an electric field) in a medium containing no solvent was one of the many intellectual basketballs constantly in the air in Bockris's lab. My assignment was to study diffusion of the individual ions in the complex-containing ($CdCl_2$ + KCl) system [7].

In contrast to the field of metallurgical silicate liquids, molten salt studies had been relatively advanced since the early part of the 20th century. The German school had studied a great many lower-melting systems. They had already shown that the Walden rule, Eq. (1.1) [8], that reliably related the equivalent conductivity Λ of aqueous solutions to their viscosities, η,

$$\Lambda\eta = \text{constant} \tag{1.1}$$

broke down seriously for molten silver halides and needed to be replaced by the "fractional" Walden rule:

$$\Lambda\eta^{\gamma} = \text{constant} \tag{1.2}$$

where γ is a constant $0 < \gamma < 1$.

The fractional Walden rule, which implied that the Arrhenius activation energy for conductivity was lower than that for viscosity, found a natural interpretation in terms of one of the ionic species ions being smaller than the other, hence capable of squeezing through smaller gaps in the condensed phase structure. This decoupling of the ionic motions reached an extreme in the case of silver salts of large polarisable anions. These were later to become important components of the "superionic" family of ionic glasses, and thus the stage was already set for the understanding of these materials, which would get much research attention in the second half of the century as electrolytes for solid state batteries. Success in this respect required a breakdown of Eq. (1.1) by some 12 orders of magnitude [9]!

Interestingly enough, the original Walden rule finds a new lease on life in current studies of ionic liquids of the ambient temperature variety, where the Walden plot, in the form log (Λ) versus log (η^{-1}) is being used as a classification diagram to distinguish "normal" ionic liquids from "poor" ionic liquids, on the one hand, and "superionic" liquids on the other hand [10, 11]. An example will be seen at the end of this chapter. The search for "superprotonic" electrolytes for fuel cell applications is in full swing at this time. Superprotonics are the holy grail of the fuel cell discipline and will briefly be considered later.

The study of complex anions was very pertinent to the Oak Ridge National Laboratory nuclear reactor program, which had also benefited from the talents of prewar displaced German physical chemists. At Oak Ridge, people were studying the "weak field" analogues of the "basic" MgO–SiO_2 metallurgical slags, represented by solutions of alkali fluorides and the Lewis acid BeF_2 (all ion charges halved relative to the MgO–SiO_2 melts). Complexation of the fluoride ions [12], to yield tetrahedral

$[BeF_4]^{2-}$ and $[Be_2F_7]^{3-}$ anions, reduced the Coulomb energy of the liquid, lowering liquidus temperatures and also lowering viscosity [13] to give fluids with the excellent heat transfer characteristics needed for a successful nuclear reactor program.

The high degree of analogy to silicate systems presented by the $LiF–BeF_2$ system was not of great interest to Oak Ridge scientists, but became the centre of attention in the East German laboratory of Vogel. Vogel et al. [14] not only determined the phase diagram but showed that, in solutions rich in BeF_2, the glass-forming solutions underwent a liquid–liquid phase separation [15] during cooling, similar to that which had been identified in silica-rich $Li_2O–SiO_2$ glasses.

A further analogy was waiting to be made, using molten chlorides closer in nature to those with which the field is currently so involved. With $ZnCl_2$ as the network glass former and pyridinium chloride as the network breaker (or "modifier"), Easteal and Angell [16] demonstrated that the glass-forming properties of the binary chloride system were highly analogous to those of the $Na_2O–SiO_2$ system.

While complex anions that could be enlarged into glass-forming networks were clearly of interest, complex cations were not to be neglected. The rare earth analogues of Humphrey Davy's crimson alkali metal–alkali halide solutions were then under study at Imperial College in the group of John Bockris's former student, John W. Tomlinson. The writer had the privilege of working under Tomlinson as the Imperial College Stanley Armstrong fellow and studied the deep scarlet solution formed by the solution of metallic cadmium in $CdCl_2$ [17]. Rather than forming the liquid equivalent of blue-purple alkali chloride crystal f-centres (lattice vacancies containing an excess electron), which was Gruen and co-workers' [18] interpretation of Humphrey Davy's crimson alkali halide solutions, the excess cadmium in $CdCl_2$ appeared to form metal dimers, $[Cd_2]^{2+}$.

1.2 VISCOSITY AND GLASS-FORMER PHENOMENOLOGY IN "SIMPLE" IONIC LIQUIDS

While it is now common knowledge that ambient temperature ionic liquids of current interest frequently supercool and vitrify, there was a time when most inorganic ionic liquid researchers would consider the formation of ionic glasses, in the absence of covalently bound networks, to be impossible.

The first evidence to the contrary was provided by Russian researchers engaged in the study of binary phase diagrams [19], who reported that in some simple salt systems there were liquid compositions that failed to crystallise during normal cooling. A useful survey of (alkaline earth + alkali metal nitrate) solutions by the German group of Thilo [20] showed this was systematically related to the relative sizes of monovalent and divalent cations and was connected to the existence in favourable systems, of very low eutectic temperatures.

The observations by Thilo et al. [20] were preceded by Dietzel and Poegel [21], who carried out a detailed study of crystallisation rates and glass formation in the now classic $(Ca(NO_3)_2 + KNO_3)$ system. They found that the composition 38% $Ca(NO_3)_2$ was particularly resistant to crystallisation, although it was well on the $Ca((NO_3)_2$-rich side of the eutectic composition. The 40:60 mole % composition in

this system (now affectionately known as CKN) has since become one of the most thoroughly investigated of all ionic liquid systems and has been the test case for sophisticated new experimental techniques. For instance, the neutron spin-echo technique [22], by means of which the intermediate scattering function needed for testing the Götze mode-coupling theory of glass-forming liquids [23] was first determined, employed CKN as the test liquid.

The finding that glasses can be formed in systems as simply constituted as CKN (two cations each with the argon electronic structure, and a small triangular anion) provided the motivation for most of this writer's researches in the physical chemistry of liquids [24].

The especially simple behaviour of the CKN system is illustrated [25, 26] by the way that a spread of precise conductivity data covering several orders of magnitude, obtained when composition and temperature are both varied, can be collapsed onto a single straight line when the data are treated using the relation now known outside the ionic liquid field as the Vogel–Fulcher–Tammann (VFT) [27–29] equation (after the independent (1921–1926) works of early authors who used it to describe the temperature dependence of viscosity for many single-component [29], as well as complex, silicate mixture compositions [28]). For the most typical glass-former transport property, the viscosity, this is expressed by:

$$\eta = \eta_0 \exp(\mathrm{B}/[T-T_0]) \tag{1.3}$$

where η_0, B, and T_0 are constants, and T_0 varies linearly with composition. (In the present author's opinion, Eq. (1.3) should be called the Tammann–Fulcher equation to recognise the weight of Tammann's contribution. After all, Vogel never studied a supercooled liquid, and the equation used by him to describe some liquid viscosities was not of the form of Eq. (1.2), but instead a much less suggestive mathematical equivalent. The idiosyncratic [30] designation, VFT equation, that the writer introduced in 1972 [31]—and which is now widespread in use—was a protest against the chronological convention, and an attempt to credit the superior understanding demonstrated in Tammann's writings of the equation's implications. T_0, of course, represents the temperature at which the viscosity would diverge on extended supercooling. It distinguishes the equation from the Arrhenius law obtained when $T_0 \rightarrow 0$ K, and implies the existence of some sort of transition that terminates the liquid state. The nature of this transition, and even its existence, has been the focus of unresolved argument among glass theorists for many decades.

The simple relation of the parameter T_0 to the experimental glass transition temperature T_g is shown in Figure 1.2. When the linear increase of T_0 is combined with Eq. (1.3), a simple relation for the conductivity at any temperature and composition is obtained [25]. This permits the data of Figure 1.1a to be collapsed to the single straight line shown in Figure 1.1b.

If B in Eq. (1.3) is replaced by the product DT_0, or T_0/F, as in Eq. (1.4a) and (1.4b),

$$\eta = \eta_0 \exp(DT_0/[T-T_0]) \tag{1.4a}$$

$$= \eta_0 \exp(T_0/F[T-T_0]) \tag{1.4b}$$

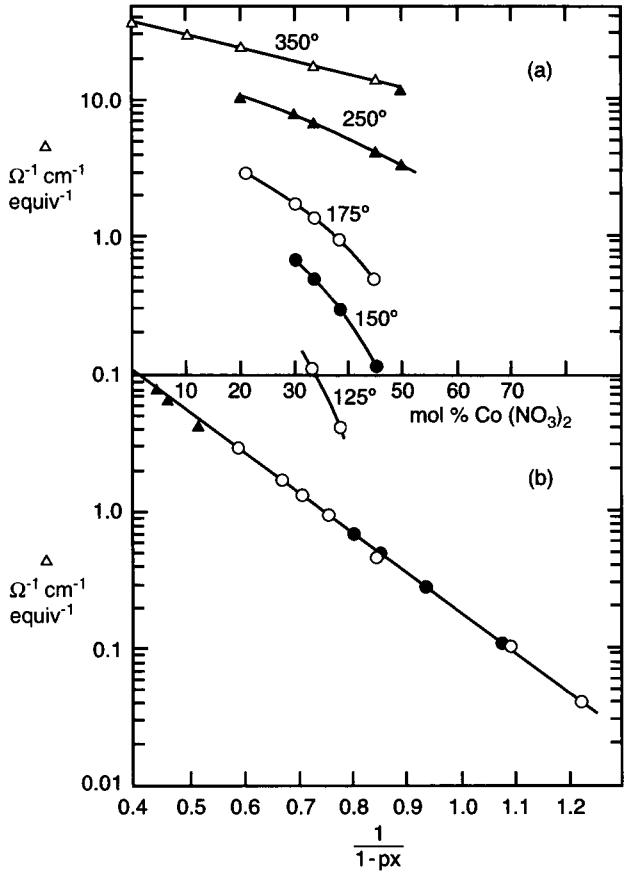

FIGURE 1.1 Simple behaviour of the physical properties of solutions in the binary system (KNO_3 + $Ca(NO_3)_2$), which is glass forming in the range 33–45% $Ca(NO_3)_2$. (a) Isotherms of conductivity versus mole % $Ca(NO_3)_2$. (b) Collapse of the data for part (a) to a single line using an equation derived from Eq. (1.3) on the assumption that T_0 is linear in composition (as demonstrated in Fig. 1.2) (From Angell [25, 26] with permission.)

then the values of the parameters D and F quantify the deviation from Arrhenius behaviour that the data exhibit. This deviation has become known as the fragility of the liquid [32] and can be represented numerically by the parameter F, although a number of other metrics are more commonly used [33]. The calcium–potassium nitrate system exhibits one of the largest values of F that has been observed (though the increase of the Arrhenius slope with decreasing temperature appears to saturate above T_g [34]). Since the dramatic breakdown of the familiar Arrhenius law is one of the most striking features of glass-forming liquids, CKN has attracted a lot of attention from investigators of the physics of glass-forming liquids. When F is large, the value of T_0 lies close to the experimental glass transition temperature, as can be seen in